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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the manufacturing method of the organic inorganic-composite-membrane coating article formed in the base surface of glass, Ceramics Sub-Division, a plastic, or metal, the constituent for organic inorganic-composite-membrane covering, and an organic inorganic-composite-membrane coating article.
[0002]
[Description of the Prior Art]The art which reforms the surface of a substrate is known by providing the organic inorganic composite membrane which has an inorganic oxide and an organic group in the surface of a glass plate and other substrates.
[0003]The substitution silicon alkoxide from which a part of silicon alkoxide and alkoxyl group were replaced by JP,H4-338137,A by the fluoro alkyl group, The glass with which the organic inorganic composite membrane which has water repellence was covered is indicated by applying to the glass substrate surface alcohol, water, and the solution that mixed acid (or base), and calcinating it.
[0004]The organic inorganic-composite-membrane coating article which has the water repellence processed with the solvent and the constituent which dissolves in a nonaqueous solvent preferably in the mixture of a perfluoro-alkyl alkyl silane and Silang (for example, tetrachlorosilicane) which can be hydrolyzed thoroughly is indicated by JP,H8-239653,A.
[0005]The organic inorganic-composite-membrane coating article which has the water repellence processed with the constituent which dissolves a chlorosilyl group content compound and a fluoro alkyl group content silane compound in alcoholic solvent is indicated by JP,H11-71682,A.
[0006]
[Problem(s) to be Solved by the Invention]The organic inorganic composite membrane in such

art applies to a substrate the solution containing the silane compound which has the silane compound and the water-repellent group which can be hydrolyzed, and is produced by what is called sol gel process to dry. In a sol gel process, since volatilization of a solvent advances in parallel with formation of oxide combination, in desiccation of 400 ** or less, detailed fine pores exist in a film, and membranous hardness is not high. In order to make this nonporous and to raise membranous hardness, calcination at 500-600 ** is indispensable, but at such a temperature, an organic group like a water-repellent group which contributes to surface treatment will decompose. Therefore, in said art, membranous desiccation or hardening was performed at the temperature of 250 ** or less, and the obtained organic inorganic composite membrane did not turn into a film which has high hardness like the oxide obtained with scorification, or Ceramics Sub-Division, for example, although the oxide was the main ingredients.

[0007]When such an organic inorganic-composite-membrane coating article is used outdoors, for example, the characteristic by which the crack was easily attached to the membrane surface and refining was carried out by extension will be lost by being put to the situation where sand is sprayed. In order to remove the adhering dust, mud, or sand, a film will get damaged and separate also by wiping the surface with cloth etc. Even when dust etc. have not adhered, by friction (for example, surface **** of the windowpane of a car with a wiper etc.) with cloth, a brush, etc. which consist of hard textiles, a small crack will be formed and degradation of the characteristic will be promoted.

[0008]This invention is made in view of the above problems, and is a thing.

the purpose -- being also alike -- it is providing the coating liquid composition for the method of manufacturing the article with which the organic inorganic composite membrane which bears, and which has high hardness and has water repellence and other functionality was covered, and this coating article for the outstanding productivity, and this coating article manufacture.

[0009]

[Means for Solving the Problem]In order to solve an aforementioned problem, as a result of repeating research wholeheartedly, this invention persons discovered hardness of organic inorganic composite membrane rose by leaps and bounds rather than having made organic inorganic composite membrane contain alkali metal ion.

[0010]Namely, a coating article which said organic inorganic composite membrane expresses an alkali metal oxide with the number of alkaline metal atoms in a coating article this invention is characterized by that comprises the following, and is characterized by the total number sum total of said alkaline metal atom and said cation atom containing 0.1 to 30%.

Base.

Organic inorganic composite membrane which replaces a part of oxygen of an oxide of owner

Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. for an oxide of a cation atom which can form oxide meshes of a net covered by the surface of the base by an organic group.

[0011]When forming an oxide film by a sol gel process generally, a metal alkoxide, for example, an alkoxide of silicon (Si), is used as a starting material in many cases. In a sol gel process, since volatilization of a solvent advances in parallel with formation of combination (siloxane bond) of metal by a dehydrating condensation reaction, for example, silicon, (Si), and oxygen (O), it becomes a porous silica film in which detailed fine pores exist in a film. Since combination of this silicon and oxygen is covalent bond nature and silicon and oxygen are combined with big binding energy, In a volatilization stage of a solvent, if a siloxane bond forms three-dimensional structure to some extent, Although a dehydrating condensation reaction progresses after that, contraction of that structure will be controlled, a portion into which water generated by a solvent, alcohol generated by a hydrolysis reaction, and a dehydrating condensation reaction volatilized will remain as fine pores, and a silanol group, an alkoxyl group, water, or alcohol will exist in these fine pores. Hardness of this porous silica film is not so high because of that porosity. When this film is heated at temperature of not less than 500 **, membranous fine pores disappear, serve as silica membrane of quality of nonporous, and have high hardness. However, since a water-repellent organic group like a fluoro alkyl group is decomposed with this cooking temperature, for example, at temperature (for example, 300 ** or less) which a water-repellent organic group does not decompose, membranous fine pores hardly disappear and, as for membranous hardness, membranous cooking temperature does not become high.
[0012]In this invention, an alkali metal oxide is introduced into organic inorganic composite membrane. Since character of an alkaline metal like ion is strong, it exists in the state of ion in a solution also in a volatilization stage of a solvent by making it dissolve into coating fluid for film formation, and making it coexist with metallic compounds (for example, silane compound) in which hydrolysis like a silicon alkoxide is possible. Since alkaline metal (M) ion is univalent, it reacts to metal hydroxyl (for example, silanol group), Metal forms for example, "$O^{-+}M$" combination as compared with combination of "Si-O-Si" which combines with oxygen (O) as eventually shown in the following formula (1) inside a film and whose directivity of combination is more nearly free when it is silicon (Si). Therefore, a skeleton of organic inorganic composite membrane which introduced an alkali metal oxide is [become] easy to change with heat as compared with a skeleton of a film which does not contain an alkali metal oxide. As a result, according to this invention, a skeleton changes with desiccation or heating of a temperature lower than decomposition temperature (250-300 **) of an organic group contained in organic inorganic composite membrane, much fine pores disappear, a film elaborates, and a film with dramatically high hardness is obtained.

[Formula 1]

**Si-O $^{-}$ $^{(1)}$ $^{+}$M (M is an alkaline metal)

[0013]The organic inorganic composite membrane in this invention can be made to contain an alkali earth metal oxide. The character of alkaline-earth metals like ion is strong like an alkaline metal. Membranous abrasion resistance can be improved further, without spoiling the cold cure characteristic by alkaline metal introduction by making an alkali earth metal oxide contain. Although the organic inorganic composite membrane in this invention contains the organic group like the after-mentioned, this organic group exists by the density higher than the inside of organic inorganic composite membrane on the surface. Addition of an alkali earth metal oxide can raise the density of the membrane surface of this organic group further, and, as a result, the function of an organic group can be improved further. For example, when an organic group is a water-repellent group, a membranous angle of contact can be made still higher by addition of an alkali earth metal oxide, waterdrop can roll, and a sex can be made still better.

[0014]In this invention, although lithium (Li), sodium (Na), potassium (K), a rubidium (Rb), caesium (Cs), and francium (Fr) are used as said alkaline metal, Li and Cs are suitably used for a Reason for that acquisition is easy in these, and solubility to both water and alcohol being high. Although calcium (Ca), magnesium (Mg), strontium (Sr), barium (Ba), radium (Ra), and beryllium (Be) are used as said alkaline-earth metals, Ca and Mg are suitably used for Reasons of there not being that acquisition is easy, solubility to both water and alcohol being high, and toxicity in these.

[0015]Since a segregation will be carried out, it will become heterogeneous and membranous hardness will fall if too conversely large [if there is not much little content of an alkali metal oxide in organic inorganic composite membrane, an effect of cold cure nature will not be acquired and], This content is 0.1 to 30% of a total of the total number sum total of a cation atom which constitutes an oxide which expresses with the number of alkaline metal atoms, and forms meshes of a net of organic inorganic composite membrane, an alkaline metal atom, and said below-mentioned alkaline-earth-metals atom, and is 1 to 25% preferably.

[0016]Since a segregation will be carried out, it will become heterogeneous and membranous hardness will fall if there is too much content of an alkali earth metal oxide in organic inorganic composite membrane, such content, A cation atom which expresses with the number of alkaline-earth-metals atoms, and constitutes a meshes-of-a-net formation inorganic oxide of organic inorganic composite membrane, It is preferred that it is 0 to 30% of the total number sum total of said alkaline metal atom and said alkaline-earth-metals atom, it is more preferred that it is 0.1 to 30%, and it is still more preferred that it is 1 to 25%. However, the sum total of content of an alkali metal oxide and an alkali earth metal oxide, It expresses with the sum total number of said alkaline metal atom and an alkaline-earth-metals atom, and it is preferred that it is 50% or less of the total number sum total of said cation atom, said alkaline metal atom, and

said alkaline-earth-metals atom.

[0017]Organic inorganic composite membrane in this invention has an oxide of a cation atom which can form oxide meshes of a net. As this cation atom, silicon, titanium, a zirconium, aluminum, germanium, tantalum, tin, antimony, cerium, a lantern, tungsten, indium, boron, etc. can be raised. In these, it is comparatively hard to produce an aggregate and a crystal during membrane formation, and since a film without a crack is easy to be obtained, silicon is used preferably.

[0018]Organic inorganic composite membrane in this invention has an oxide of a cation atom which can form oxide meshes of a net, and a part of oxygen of the oxide is replaced by an organic group. Especially as this organic group, although it does not limit, a univalent organic group is preferred, For example, to alkyl groups, such as a methyl group, an ethyl group, and an isopropyl group, a phenyl group, a vinyl group, an aminopropyl group, an acrylic group, an epoxy group, a polyether group, and a pan. A part or all of hydrogen of hydrocarbon can mention a fluoro alkyl group, a chloro alkyl group, etc. which were replaced with fluoride or chlorine. In these, an alkyl group and the fluoro alkyl group can give water repellence to a film, the methyl group can give low friction nature to a film, and an aminopropyl group and the polyether group can give hydrophilic nature to the surface, for example.

[0019]These organic groups exist in a form combined with a cation atom (example; silicon atom) of an inorganic oxide (for example, SiO_2) which forms the meshes of a net in organic inorganic composite membrane. Since membranous intensity will decrease if too conversely large [if content of this organic group is too small not much, it will not contribute to refining of a base surface and a film will not exhibit a predetermined function, and], It is preferred that it is less than twice in 0.001 or more times of the total number sum total of a cation atom of an inorganic oxide which expresses with the number of an organic group and forms the meshes of a net in organic inorganic composite membrane, said alkaline metal atom, and an alkaline-earth-metals atom. They are 0.01 time - 1 time more preferably. Although this organic group may be uniformly distributed over a membranous thickness direction, even if it serves as an inclination presentation film to which that concentration changes from the interface side with a base toward an outer surface, it is not cared about. For example, in order to give a water-repellent function, when an alkyl group and/or a fluoro alkyl group in a film are made to contain so that the number may turn into 50 to 100% of the total number of an organic group, film hardness and an interval serve as a water-repellent membrane with high durable performance, and are still more preferred.

[0020]By this invention, thus, alkali metal ion, Or by including alkali metal ion and alkaline earth metal ion, also with desiccation or heating below decomposition temperature of an organic group which contributes to surface treatment, a film which has the high hardness which was not obtained conventionally was obtained, and, as a result, durable performance of organic

inorganic composite membrane improved by leaps and bounds.

[0021]Such cold cure nature is not checked even when introducing a transition metal ion etc. further into a film for the purpose of, for example, adding further a function which controls a membranous refractive index or controls visible light transmittance in addition to the refining characteristic by an organic group. Namely, by making a metal ion and an alkali metal oxide (or both an alkali metal oxide and an alkali earth metal oxide) which reveal the target function live together with desiccation or heating of 300 ** or less of temperature. Hardness is dramatically high and it can be considered as a compound function film having the refining characteristic by an organic group, and a function by a metal ion. For example, organic inorganic composite membrane colored by adding cobalt oxide, iron oxide, nickel oxide, and copper oxide can be obtained.

[0022]As for an organic molecule except being contained as said organic group, although it is possible to make it contain like said bipolar membrane also about organic molecules, such as organic coloring matter, it is preferred to carry out to 5 or less % of the weight to film weight. It is because cold cure ability may be spoiled if it adds exceeding this.

[0023]If membranous thickness is too large not much, film hardness will fall easily, and if too not much small, an effect of surface treatment will not be acquired. Therefore, 5-200 nm of thickness [5-100 nm of] is 5-50 nm still more preferably more preferably.

[0024]An organic metallic compound in which this invention has (A) non-hydrolytic organic group, (B) They are acid, the (C) alkali metal compound, and a constituent for covering that contains a compound in which condensation polymerization is completely possible or, in which hydrolyzed condensation polymerization is possible, and (D) (E) alkaline earth metal compound if needed, respectively.

[0025]the number of cation atoms excluding [the aforementioned (A) ingredient] the organic group -- the sum total (however, except for a cation atom in an organic group) of the number of cation atoms of the aforementioned (A) ingredient, the (C) ingredient, the (D) ingredient, and the (E) ingredient the following -- it is the same -- it is preferred to receive, and to contain so that it may become 0.1 to 99.8%, and it is more preferred to contain so that it may become 1.0 to 90%. As opposed to the sum total of the number of cation atoms excluding [the number of the alkaline metal atoms] an organic group of the aforementioned (A) ingredient, the (C) ingredient, the (D) ingredient, and the (E) ingredient in the aforementioned (C) ingredient, Containing is preferred so that it may become 0.1 to 30%, and it is more preferred to contain so that it may become 1 to 25%. The aforementioned (D) ingredient is an ingredient which strengthens combination with a film and a substrate more. (D) As for an ingredient, containing is preferred so that the number of cation atoms except the organic group may be 0 to 99.7% to the sum total of the number of cation atoms except an organic group of the aforementioned (A) ingredient, the (C) ingredient, the (D) ingredient, and the (E) ingredient, and containing 1 to

88% is more preferred. And the aforementioned (E) ingredient receives the sum total of the number of cation atoms excluding [the number of the alkaline metal atoms] an organic group of the aforementioned (A) ingredient, the (C) ingredient, the (D) ingredient, and the (E) ingredient, Containing is preferred so that it may become 0.1 to 30%, and it is more preferred to contain so that it may become 1 to 25%.

[0026]Although the (D) ingredient in this invention is not an essential ingredient, it is possible for you to make it dissolve in alcohol which is a common solvent as a (D) ingredient, and a compound in which hydrolysis and condensation polymerization are completely possible, or a compound in which condensation polymerization is completely possible can use it extensively. A compound in which hydrolysis and condensation polymerization are completely possible is a compound which a hydrolytic basis combined with a cation atom, and is a compound with the number equal to a valence of a cation atom of hydrolytic bases. A compound in which condensation polymerization is completely possible is a compound which a hydroxyl group combined with a cation atom, and is a compound with the number equal to a valence of a cation atom of hydroxyl groups. (D) a cation atom (silicon.) which can form oxide meshes of a net as an ingredient, for example Alkoxides, such as titanium, a zirconium, aluminum, germanium, tantalum, gallium, tin, antimony, cerium, a lantern, tungsten, indium, a scandium, yttrium, and boron, hydroxide, a chloride, a nitrate, etc. can be mentioned. What is necessary is just to add by chelating by beta diketones, such as an acetylacetone, like alkoxides, such as titanium, a zirconium, aluminum, and boron, when a solution with it is hard to be obtained. [very high reactivity and] [homogeneous in addition of only this] In the case of a compound which melts into water although it does not melt into alcohol, water may be added if needed. As an ingredient, more specifically (D) Silicontetraalkoxides, such as a tetramethoxy silane and a tetraethoxysilane, Titaniumtetraalkoxides, such as titanium tetraisopropoxide and titaniumtetrabutoxide, Zirconium tetra isopropoxide, zirconiumtetraethoxide, Zirconiumtetraalkoxides, such as zirconiumtetrabutoxide, H_3BO_3, $ZrOCl_2$, $ZrO(NO_3)_2$, $AlCl_3$, $GeCl_4$, $TaCl_5$, $GaCl_3$, $InCl_3$, $ScCl_3$, YCl_3, $LaCl_3$, $CeCl_3$, aluminum$(NO_3)_3$, $Ga(NO_3)_3$, $In(NO_3)_3$, $SbCl_3$, WCl_6, Solubility [as opposed to water or alcohol in compounds, such as $Sc(NO_3)_3$, $Y(NO_3)_3$, $La(NO_3)_3$, and $Ce(NO_3)_3$,] can use it conveniently highly.

[0027]As an alkali metal compound which is the aforementioned (C) ingredient, it is possible for you to make it dissolve in alcohol, for example, a chloride of an alkaline metal (lithium, sodium, potassium, a rubidium, caesium, francium), a nitrate, etc. are used. More specifically, solubility [as opposed to water or alcohol in metallic compounds, such as LiCl, NaCl, KCl, RbCl, CsCl, and FrCl,] can use it conveniently highly.

[0028]Although an alkaline earth metal compound which is the aforementioned (E) ingredient is not an essential ingredient, as a (E) ingredient, It is possible for you to make it dissolve in

alcohol, for example, a chloride of alkaline-earth metals (beryllium, magnesium, calcium, strontium, barium, radium), a nitrate, etc. are used. More specifically $BeCl_2$, $MgCl_2$, $Mg(NO_3)_2$, Solubility [as opposed to water or alcohol in metallic compounds, such as $CaCl_2$, $Ca(NO_3)_2$, $SrCl_2$, $BaCl_2$, $RaCl_2$, and $Ba(NO_3)_2$,] can use it conveniently highly.

[0029]As an organic metallic compound which has a non-hydrolytic organic group in this invention which is the (A) ingredient, For example, metallic compounds of the compounds indicated as the aforementioned (D) ingredient, That is, a compound in which some anions of a compound of silicon, titanium, a zirconium, aluminum, germanium, tantalum, tin, antimony, cerium, a lantern, tungsten, and indium were replaced by an organic group of un-hydrolyzing nature can use it conveniently. Each of these metal is the cation atoms which can form oxide meshes of a net. Although it does not limit, especially as an organic group of un-hydrolyzing nature A methyl group, Alkyl groups, such as an ethyl group and an isopropyl group, a phenyl group, a vinyl group, an aminopropyl group, an acrylic group, an epoxy group, a fluoro alkyl group by which a part or all of hydrogen of hydrocarbon was replaced further, a chloro alkyl group, etc. are mentioned. These organic groups remain in organic inorganic composite membrane, and give functionality, such as water repellence, low friction nature, and hydrophilic nature, to a film. Since an organic silicon compound which has such a nondegradable organic group is obtained as a comparatively stable compound, it can be used especially preferably.

[0030]For example, as a silane compound which has an alkyl group, $CH_3(CH_2)_{18}SiCl_3$, $CH_3(CH_2)_{16}SiCl_3$, $CH_3(CH_2)_2SiCl_3$, $CH_3CH_2SiCl_3$, $(CH_3CH_2)_2SiCl_2$ and $(CH_3CH_2)_3SiCl$, CH_3SiCl_3, $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, $CH_3(CH_2)_{18}Si(OCH_3)_3$ like $CH_3(CH_2)_{16}Si(OCH_3)_3$, $CH_3(CH_2)_8Si(OCH_3)_3$, $CH_3(CH_2)_7Si(OCH_3)_3$, $CH_3(CH_2)_2Si(OCH_3)_3$, $CH_3CH_2Si(OCH_3)_3$, $(CH_3CH_2)_2Si(OCH_3)_2$, $(CH_3CH_2)_3SiOCH_3$, $CH_3Si(OCH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $(CH_3)_3SiOCH_3$, $CH_3(CH_2)_{18}Si(OC_2H_5)_3$, $CH_3(CH_2)_{16}Si(OC_2H_5)_3$, $CH_3(CH_2)_8Si(OC_2H_5)_3$, $CH_3(CH_2)_7Si(OC_2H_5)_3$, $CH_3(CH_2)_2Si(OC_2H_5)_3$, $CH_3CH_2Si(OC_2H_5)_3$, $(CH_3CH_2)_2Si(OC_2H_5)_2$, $(CH_3CH_2)_3SiOC_2H_5$, $CH_3Si(OC_2H_5)_3$, $(CH_3)_2Si(OC_2H_5)_2$ and $(CH_3)_3SiOC_2H_5$, $CH_3O(Si(CH_3)_2O)_nCH_3$ -- (-- here -- n -- an end methoxyl polydimethyl siloxane like 2 - 2000). $HO(Si(CH_3)_2O)_nH$ -- (-- as for n, an end silanol polydimethyl siloxane like 2 - 2000), etc. are mentioned here.

[0031]As a silane compound which has a FUROORO alkyl group, $CF_3(CF_2)_9(CH_2)_2SiCl_3$, $CF_3(CF_2)_7(CH_2)_2SiCl_3$, $CF_3(CF_2)_5(CH_2)_2SiCl_3$, $CF_3(CF_2)_3(CH_2)_2SiCl_3$, FUROORO alkyl

group content trichlorosilane;$CF_3(CF_2)_9(CH_2)_2Si(OCH_3)_3$ like $CF_3CF_2(CH_2)_2SiCl_3$ and $CF_3(CH_2)_2SiCl_3$, $CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3$, $CF_3(CF_2)_5(CH_2)_2Si(OCH_3)_3$, $CF_3(CF_2)_3(CH_2)_2Si(OCH_3)_3$, $CF_3CF_2(CH_2)_2Si(OCH_3)_3$, $CF_3(CH_2)_2Si(OCH_3)_3$, and ** -- FUROORO alkyl group content trialkoxysilane [like] is mentioned.

[0032]Although a water-repellent function can be given to a base material surface by using these FUROORO alkyl group content silane compound, It can be considered as a film which combines outstanding water-repellent performance and durable performance by using trichlorosilane, trialkoxysilane, etc. containing a FUROORO alkyl group which has ten or more fluorine atoms. Especially, $CF_3.(CF_2)_7.(CH_2)_2Si(OCH_3)_3$ (heptadecafluorodecyl trimethoxysilane) and $CF_3(CF_2)_7(CH_2)_2SiCl_3$(heptadecafluorodecyltrichlorosilane) can use it preferably.

[0033]Although it is not limited, since especially acid that is the (B) ingredient in a constituent for covering in this invention can be used as a film with high hardness as what evaporates during desiccation and cannot remain in a film easily, it is preferred. For example, chloride, nitric acid, acetic acid, fluoric acid, formic acid, trifluoroacetic acid, etc. are mentioned. Especially, also when having and dealing with a high degree of electrolytic dissociation and volatility, especially comparatively safe chloride is preferred. As for the aforementioned (B) ingredient, it is preferred to contain 0.001-3 N.

[0034]In the boiling point in atmospheric pressure, as a solvent in this invention, a solvent 150 ** or less can use it extensively. For example, hexane, toluene, hydrocarbon like cyclohexane, a methyl chloride, A carbon tetrachloride, halogenated hydrocarbon like trichloroethylene, acetone, ketone like methyl ethyl ketone, a nitrogen-containing compound like diethylamine, ester like ethyl acetate, and alcohols can be used. Although alcoholic solvent is used preferably, for example, methanol, ethanol, 1-propanol, 2-propanol, butyl alcohol, amyl alcohol, etc. can be mentioned also in these, Since the vapor rate [in / in chain saturation monohydric alcohol whose carbon number like methanol, ethanol, 1-propanol, and 2-propanol is three or less / ordinary temperature] is large in them, it is used still more preferably.

[0035]Said alcohol may contain 0 % of the weight or more and 50% of the weight or less of water. Although 0.2% of the weight or more of moisture is usually contained in commercial best alcohol, in this invention, it can use preferably, without carrying out processing which leads to cost hikes, such as dehydrating treatment. When adding a metallic raw material, beforehand, metallic compounds may be dissolved in water and it may add, or in order to control a drying rate and viscosity of liquid, others and a solvent may be added. It is preferred that quantity of chain saturation monohydric alcohol whose carbon number mentioned above also on that occasion is three or less is 10 % of the weight or more to the amount of solvents. A homogeneous and transparent film may not be obtained in quantity not more than this.

[0036]In a constituent for covering (coating solution) containing aforementioned (A) - (E) ingredient, as for the aforementioned (A) ingredient and the (D) ingredient, a hydrolysis reaction and a dehydrating condensation reaction advance with water of some in a catalyst (B) ingredient and a solvent. If a lot of water exists in coating fluid, a hydrolysis reaction of the above (A) and the (D) ingredient and a dehydrating condensation reaction will be promoted, and pot life of coating fluid will become short, and it will become easy to produce nonuniformity of thickness in the case of desiccation after spreading of coating fluid. Therefore, in order to lengthen pot life of a solution and to lose nonuniformity of thickness in the case of desiccation after spreading, the smaller possible one of concentration of water in a coating solution is preferred. setting to this invention, since 0.2% of the weight or more of moisture is usually contained in commercial alcohol -- this moisture -- although it comes out enough, when adding water separately, as for concentration of water in coating fluid, it is preferred that it is 0 to 5 % of the weight, and it is still more preferred that it is 0 to 2 % of the weight. Even if concentration of water in coating fluid is zero, since moisture in the air is absorbed by coating film after being applied to a substrate, a hydrolysis reaction is not checked.
[0037]Although a coating method in particular in this invention is not limited, For example, dip coating, flow coating, curtain coating, spin coating, spray coating, bar coating, roll coating, brush coating coating, etc. can be illustrated.
[0038]Spreading in this invention is performed by 0-40 **, for example, a room temperature, in atmosphere of 40% or less of relative humidity. Desiccation after spreading is performed by 0-40 **, for example, a room temperature, for [10 seconds -] 20 minutes in atmosphere of 40% or less of relative humidity. It may heat for [for / 30 seconds / -] 10 minutes at temperature of 300 ** or less if needed more highly than a room temperature after that. Therefore, a film of high hardness which has functionality peculiar to an organic group can be obtained, without an organic group which constitutes a film decomposing. When an organic group of functionality is a water-repellent group and it heats in temperature of 300 ** or less after the above-mentioned spreading more highly than a room temperature, it is preferred that ****** of a film obtained performs desiccation at a room temperature after spreading since **** and ultraviolet resistance fall easily.
[0039]As a substrate in this invention, a thing of shape of transparent or opaque plates, such as glass, Ceramics Sub-Division, a plastic, or metal, a rod-like structure, and other versatility is mentioned. On the surface of a substrate, when there are few hydrophilic radicals, process and hydrophilic-nature-ize the surface in plasma or corona atmosphere which contains oxygen beforehand, or, Or after irradiating with ultraviolet rays of wavelength near 200-300 nm in atmosphere which includes a base material surface for oxygen and performing hydrophilic nature-ized processing, it is preferred to perform a surface treatment.
[0040]

[Embodiment of the Invention]Working example is raised to below and an embodiment of the invention is concretely described to it.

[working example 1] -- heptadecafluorodecyl trimethoxysilane ($CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3$ and the product made from Shin-etsu silicone.) it may be called the following "FAS" -- 0.2 g and a tetraethoxysilane ($Si(OCH_2CH_3)_4$ and the product made from Shin-etsu silicone.) Added agitating 0.6 g, the lithium chloride 0.00947g, and 2 g of concentrated hydrochloric acid (35 % of the weight) which may be called following "TEOS" to 999.19 g ethanol (0.35 % of the weight of water content), FAS and TEOS were made to hydrolyze, and coating fluid was obtained. Those total quantities are made into 100-mol % for the content of FAS and TEOS which are the metallic compounds in coating fluid, and a lithium chloride, and a molar fraction is shown in Table 1. This coating fluid on the surface of the glass substrate (3.4 mm x 150x150 mm) of the washed soda-lime-silicate-glass presentation, It applied by the flow coat method at 30% of relative humidity, and a room temperature (20 **), and the organic inorganic-composite-membrane covering glass plate which made the water-repellent membrane about 40 nm thick cover was obtained by making it dry at 30% of relative humidity, and a room temperature (20 **) for about 1 minute. The molar fraction of the alkaline metal atom to the sum total of the cation atom (silicon) and alkaline metal atom (lithium) which constitute the inorganic oxide of the obtained organic inorganic composite membrane was as being shown in Table 1.

[0041]About the organic inorganic-composite-membrane covering glass plate which has the obtained water-repellent function, the angle of contact of water was measured as a static contact angle by waterdrop with a weight of 2 mg using the angle-of-contact meter (CA-DT, product made from Harmony Interface Science). It means that static water repellence is excellent, so that the value of this angle of contact is large. As a measure which shows the performance (waterdrop rolling sex) for which waterdrop rolls the surface of the covering glass plate which has water repellence, Put the waterdrop of 50microl on the surface of the covering glass plate arranged horizontally, the glass plate was made to incline gradually, and the angle of gradient (critical slope angle) of the glass plate in case the waterdrop put on the surface begins to roll was measured. It means that the raindrop which the dynamic water-repellent performance is excellent in, for example, adhered to the windshield window of the car under run disperses easily, and a driver's field of view is not barred, so that a critical slope angle is small.

[0042]Evaluation of membranous hardness was performed by measuring the static contact angle by waterdrop with a weight of 2 mg which performed wear 100 times and carried out point ** by 250-g load to an organic inorganic-composite-membrane covering glass plate using the commercial Taber wear test.

[0043]The angle of contact of the organic inorganic-composite-membrane film which has a

water-repellent function, and the angle of contact before and behind the Taber wear test are shown in Table 2. About the obtained film, the angle of contact before the Taber examination was as large as 108 degrees, it is 90 degrees, and the angle of contact after the Taber examination was before and after the Taber examination, and was small, and film hardness was a very high film. [of reduction in an angle of contact] ****** expressed **** with the critical slope angle, and was 8 times.

[0044][Working example 2-10] The organic inorganic-composite-membrane covering glass which has a water-repellent function like working example 1 was obtained except having changed the raw material in the coating fluid of working example 1 and ingredient ratio of metallic compounds, respectively, as shown in Table 1. The range of the thickness of organic inorganic composite membrane of all of working example 2-10 was 5-50 nm. The molar fraction of the alkaline metal atom or alkaline-earth-metals atom to the sum total of the cation atom, alkaline metal atom, and alkaline-earth-metals atom which constitute the presentation of the cation of the obtained film, i.e., the inorganic oxide meshes of a net of organic inorganic composite membrane, was as being shown in Table 1. The result measured like working example 1 is shown in Table 2.

[0045]The angle of contact before the Taber examination of each obtained film was large, and the fall of the angle of contact after the Taber examination was a small film with high hardness. When working example 3 which does not contain an alkali earth metal oxide is compared with working example 4 which replaced some alkali metal oxides of working example 3 with the alkali earth metal oxide, it turns out that abrasion resistance and waterdrop roll [the direction of working example 4] as compared with working example 3, and the sex is excellent.

[0046][Comparative examples 1-5] The organic inorganic-composite-membrane covering glass which has a water-repellent function like working example 1 was obtained except having changed the raw material in the coating fluid of working example 1 and addition of metallic compounds, respectively, as shown in Table 1. The presentation of the cation of the obtained film was as being shown in Table 1. The result measured like working example 1 is shown in Table 2.

[0047]The obtained film had the large fall of the angle of contact after the Taber examination, although the angle of contact before the Taber examination was large, the water-repellent performance was almost lost and film hardness was dramatically low.

[0048][working example 11] -- as the metallic compounds which have a nonresponsive organic group in the coating fluid of working example 1 -- an end silanol polydimethyl siloxane (the product made from Gelest.) The average molecular weight 4200 was used and the organic inorganic-composite-membrane covering glass which has a low friction function like working example 1 was obtained except having changed the raw material and addition of metallic compounds, respectively, as shown in Table 1. However, an ingredient ratio and each molar

fraction express the content of the end silanol polydimethyl siloxane (average molecular weight 4200) with the number of mols converted into SiO_2. The presentation of the cation of the obtained film was as being shown in Table 1.

[0049]When the dynamic friction coefficient of paper and a film surface was measured using the surface measurement machine made from the new east science "HEIDON-14", as for the coefficient of friction, it turned out that the 0.1 or less surface where frictional resistance is dramatically small is obtained. As the obtained film was shown in Table 2, the angle of contact before the Taber examination was large, and the fall of the angle of contact after the Taber examination was a small film with high hardness. When the coefficient of friction was measured after the Taber examination, the coefficient of friction was 0.1 or less very small value like Taber examination before.

[0050][Comparative example 6] Both the amount of LiCl used in the coating fluid of working example 9, and $MgCl_2$ used and $6H_2O$ is made into zero, The organic inorganic-composite-membrane covering glass which has a low friction function like working example 9 was obtained except having changed DMS and TEOS, as shown in Table 1. The obtained film had the large fall of the angle of contact after the Taber examination, although the angle of contact before the Taber examination was large, the water-repellent performance was almost lost and film hardness was dramatically low.

[0051]Like working example 9, when the dynamic friction coefficient of paper and a film surface was measured before the Taber examination and after the Taber examination, the coefficient of friction after the Taber examination of that from which the 0.1 or less surface where frictional resistance is dramatically small is obtained as for the coefficient of friction before the Taber examination rose to 0.5.

[0052]

[Table 1]

---------- ---------- metallic-compounds raw material (mol %) Ingredient ratio alkaline metal alkaline-earth metals (mole ratio) Seed Content Seed Content (mol %) ----------. Working example 1 FAS/TEOS/LiCl 10/83/7. Li 7 - 02 FAS/TEOS/CsCl. 5/87/8 Cs 8 - 03 FAS/TEOS/LiCl 10/80/10 Li 10 - 04 FAS/TEOS/LiCl/$MgCl_2$ and $6H_2O$ 10/80/7/3 Li 7 Mg. 35 . FAS/LiCl/$CaCl_2$and$2H_2O$. 98/1/1 Li 1 Ca 16 FAS/CsCl/$MgCl_2$ and $6H_2O$ 50/25/25 Cs 25 Mg 257 FAS/TEOS/CsCl/$CaCl_2$ and $6H_2O$. 10/88/1/1 Cs 1 Ca 18. FAS/$ZrOCl_2$, and $8H_2O$/KCl. 10/80/10 K 10 -09 FAS/H_3BO_3/NaCl/$CaCl_2$ and $2H_2O$ 50/40/5/5 Na 5 Ca 510 FAS/LiCl 95/5 Li 5 -. 011 DMS/TEOS/LiCl/$MgCl_2$ and$6H_2O$ 1/89/7/3 Li. 7 Mg 3 comparative-example 1 FAS 100 -. 0 - 02 FAS/TEOS 10/90. - 0 - 03 FAS/TEOS/LiCl. 10/50/40 Li 40 - 04. FAS/TEOS/CsCl/$MgCl_2$ and $6H_2O$ 5/15/40/40 Cs 40 Mg 405 FAS/TEOS/$CaCl_2$ and

$6H_2O$ 10/80/10 - 0 Ca. 106 DMS/TEOS 1/99 - 0 - 0. ----------. * FAS:$F(CF_2)_8(CH_2)_2Si(OCH_3)_3$, TEOS:$Si(OC_2H_5)_4$, DMS : end silanol polydimethyl siloxane (average molecular weight 4,200)

[0053]

[Table 2]

---------- ---------- wear test enclitic antenna (degree) Angle-of-contact (degree) critical slope angle after a wear test (degree)

----------. Working example 1108 90 Eight working example 2 108. 95 Seven working example 3 108 85 Six working example 4. 108 894 working example 5 108 91 Six working example 6. 108 96 Six working example 7 108 98. Five working example 8108 92 Eight working example 9 108. 90 Eight working example 10 107 88 Nine working example 11 100 884 comparative examples 1 108 60 Ten comparative examples 2 108 73 Nine comparative examples 3 108 75 Ten comparative examples 4 108 78 Twelve comparative examples 5 108 76 13 comparative examples 6 100 78 10. ----------[0054]

[Effect of the Invention]As explained above, according to this invention, hardness can consider it as the organic inorganic composite membrane which improved by leaps and bounds by making organic inorganic composite membrane contain alkali metal ion.While raising membranous hardness further by making alkaline earth metal ion contain with alkali metal ion, the functionality of an organic group can be improved further.

[Translation done.]